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Contributions
to
The Knowledge of the Electrolysis
of
Aqueous Solutions of Vanadium Salts

BY

SIEGFRIED FISCHER, Jr.

THE UNIVERSITY OF CALIFORNIA

Contributions
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Submitted in Partial Fulfilment of the Requirements for the Degree of
Doctor of Philosophy, in the Faculty of Pure Science,
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CONTRIBUTIONS TO THE KNOWLEDGE OF THE ELECTROLYSIS OF AQUEOUS SOLUTIONS OF VANADIUM SALTS.

By SIEGFRIED FISCHER, JR.

INTRODUCTION—LITERATURE ON ELECTROLYTIC VANADIUM.

Previous to 1882, very little electrolytic work was done on vanadium, but since then much interest has developed in this field. Electrolytic processes may be divided into (1), those using an aqueous electrolyte, and (2), those using a non-aqueous or fused electrolyte. The electrolytic processes for obtaining metallic vanadium, using either aqueous or fused electrolytes, are very few, and most are of theoretical value only. The literature on the subject is very scant, and much of the data reported lacks accuracy.

It is the object of this thesis to determine whether or not it is possible to obtain metallic vanadium from aqueous solutions of its salts.

Electrolysis of Vanadium Electrolytes.

The literature on electrolytic processes for obtaining metallic vanadium is very scarce, but a considerable amount of work has been done by various scientists on the electrolytic behavior of vanadium compounds. The work is of importance, because in treating an ore or a vanadium product by electrolysis, the vanadium will always be in solution as a compound, which must be decomposed by the electric current. The literature may be conveniently divided into

1. General Literature on Electrolysis of Vanadium.
2. Electrolysis of Aqueous Solutions of Vanadium Salts for obtaining Metallic Vanadium.

1. *General Literature.* Der Zustand Einiger Übersaüren und ihrer Salze (the condition of some super acids and their salts in

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solution), in the "Zeitschrift für physikalische Chem.," **43** (1903), 160-178. L. Pissarjewsky studied the conductivity, behavior and composition of the potassium salts of the acids HVO_4 and $H_8V_6O_{26}$, and found that these compounds are much too complex to yield metallic vanadium on electrolysis, but simply an oxide.

According to L. Marino—Über das elektromotorische Verhalten des Vanadins (about the electromotive behavior of vanadium), "Zeitschrift für anorganische Chemie," **39** (1904), 152-169, the lower oxides of vanadium behave like those of chromium, while its higher oxides resemble those of phosphorus and arsenic. If vanadium is used as an anode it acts as a reducing agent in solutions of neutral salts of silver, gold, platinum and iridium, reducing the salts to the metallic state, on connecting the anode and cathode leads, while $Cu^{\cdot\cdot}$, $Hg^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ ions are only partially reduced to $Cu^{\cdot}$, $Hg^{\cdot}$ and $Fe^{\cdot\cdot}$. Vanadium exerts no reducing action on $Zu^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Ni^{\cdot\cdot}$ and $Pb^{\cdot\cdot}$. The vanadium enters the solution anodically as tetra-valent ions ($V^{\cdot\cdot\cdot\cdot}$). Marino has shown experimentally that, in an alkaline solution, vanadium enters solution as penta-valent ions ($V^{\cdot\cdot\cdot\cdot\cdot}$), while in an acid solution it dissolves as tetravalent ions ($V^{\cdot\cdot\cdot\cdot}$). The potential for the reaction $V \rightarrow V^{\cdot\cdot\cdot\cdot}$ was found to be approximately —0.3 to —0.4 volt. The article contains much experimental data, but unfortunately they lack accuracy, due to the experiments being conducted with vanadium which contained 8.66 percent carbon.

Muthmann and Frauenberger showed that vanadium under certain conditions possessed passivity. Pure vanadium in a normal solution of potassium hydroxide shows at the beginning a potential of —0.13 volt; but after ten minutes a maximum value was obtained, namely 0.737 volt. This property of passivity is shown more or less after treating the vanadium with oxidizing agents or after anodic polarization. ("Berichte der königlichen bayrischen Akadamie der Wissenschaften zu München.")

Under "Vanadium," in Abegg's "Handbuch der anorganischen Chemie," Vol. III, 683-788, is found valuable information regarding the behavior of the various vanadium ions. Tetravalent compounds may show either acid or basic properties. The acid compounds have formula VX_4, while the basic are of the type VOX_2. Under this latter type of ion comes the vanadyl-ion ($VO^{\cdot\cdot}$) and the divanadyl-ion $(V_2O_2)^{\cdot\cdot\cdot\cdot}$. The cathions (($V^{\cdot\cdot\cdot\cdot}$) or

$V(OH)^{\cdot\cdot\cdot}$ show weak electric but strong hydrolytic properties. The trivalent ion ($V^{\cdot\cdot\cdot}$) shows strong positive properties. It is different from the ions of the other metals of the same periodic group, as it does not form the compound VH_3. The electropositive property of the tri-valent ($V^{\cdot\cdot\cdot}$) ion is not very great, because this ion very readily forms double salts, similar to $Al^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$ and $Mo^{\cdot\cdot\cdot}$. The di-valent ion ($V^{\cdot\cdot}$) possesses still stronger positive character. It forms double salts with $FeSO_4$ and $MgSO_4$, strongly resembling the magnesium group of metals. The di-valent ion is very readily oxidized, and in its reducing power reminds one of the $Cr^{\cdot\cdot}$ ion.

In a dissertation entitled "Measurements of the reduction potential of solutions of diverse solutes forming vanadium compounds," published in Leipzig in 1906, T. F. Rutter gives the results on the determination of the electromotive behavior of the chains, $V^{\cdot\cdot} \rightarrow V^{\cdot\cdot\cdot}$, $V^{\cdot\cdot\cdot} \rightarrow V^{\cdot\cdot\cdot\cdot}$, and $V^{\cdot\cdot\cdot\cdot} \rightarrow V^{\cdot\cdot\cdot\cdot\cdot}$ from solutions containing V^{II} and V^{III}, V^{III} and V^{IV}, and V^{IV} and V^{V} compounds in changeable quantities. The solutions investigated were compared with a mercuro-sulphate electrode in a 0.5 normal H_2SO_4 solution of potential 0.679 volt. The results obtained are as follows:

$$V^{\cdot\cdot} \rightarrow V^{\cdot\cdot\cdot}$$

0.1n V^{II}; 0.5n H_2SO_4 (free from V^{III})	Potential	0.909	volts
0.05n V^{II}; 0.05n V^{III}; 0.5n H_2SO_4	"	0.889	"
0.033n V^{II}; 0.066n V^{III}; 0.5n H_2SO_4	"	0.881	"
0.025n V^{II}; 0.075 V^{III}; 0.5n H_2SO_4	"	0.875	"
0.1n V^{III}; 0.5n H_2SO_4 (free from V^{II})	"	0.464	"

(Mercury electrode used was positive.)

$$V^{\cdot\cdot\cdot} \rightarrow V^{\cdot\cdot\cdot\cdot}$$

0.1n V^{III} (free from V^{II} and V^{V})	Potential	0.462	volts
0.075n V^{III}; 0.025n V^{IV}	"	0.397	"
0.05n V^{III}; 0.05n V^{II}	"	0.373	"
0.025n V^{III}; 0.075n V^{II}	"	0.363	"
0.1n V^{IV} (free from V^{III} and V^{V})	"	0.051	"

(Mercury electrode used was positive.)

$$V^{\cdot\cdot\cdot\cdot} \rightarrow V^{\cdot\cdot\cdot\cdot\cdot}$$

0.1n V^{IV} (free from V^{III} and V^{IV})	Potential	0.051	volts

(Mercury electrode, used positively.)

0.05n V^{IV}; 0.05n V^{V}	Potential	0.241	volts
0.1n V^{V}; 0.5n H_2SO_4 (free from V^{IV})	"	0.462	"

(Last two experiments, mercury electrode used negatively.)

Rutter also found that vanadium of its own accord could form ions of the type $VO^{\cdot\cdot}$ from $V^{\cdot\cdot\cdot\cdot}$; VO_2'', VO_3', and V_6O_{17}'''': Also if the ratio of ($V^{II} \cdot V^{III} = 0.05 \cdot 0.05$) and ($V^{III} \cdot V^{IV} = 0.05 : 0.05$) existed, then the single potentials are respectively + 0.21 and — 0.30. This means that the tendency to form V^{II} to V^{III} is greater than the tendency to change H to $H^{\cdot}$; and the potential to change V^{III} to V^{IV} is greater than that to change Ag to $Ag^{\cdot}$: therefore, vanado-salts liberate hydrogen, and vanadi-salts liberate silver or copper of the solution of copper sulphate used is concentrated and heat applied. Vanadyl salts, according to the author are very weak reducing agents, they being readily oxidized by permanganic acid, chromic acid and hydrogen peroxide, slowly by persulphates, and only slightly by iodine and bromine. Rutter also established the fact that various oxides of vanadium immediately come to an equilibrium. Further information on this subject may be found in an article published by the same author in the "Zeitschrift für anorganische Chemie," **52**, 368-396, on "The Contribution to the Knowledge of the Compounds of Vanadium." This article deals in detail with the extract given from his thesis.

Stahler and Wirthwein prepared vanadic salts $(V)^{\cdot\cdot\cdot}$ and followed the progress of reduction by titrating part of the electrolyte at different stages of the experiments with potassium permanganate ("Berichte," **38**, 3978).

A. Bültemann quotes the work of Piccini and Brizzi who, in the "Zeitschrift für anorganische Chemie," **11**, 106, and **19**, 394, published two articles on the reduction of penta- and tetra-valent vanadium salts by means of electrolysis. Both articles show that the penta- and tetra-valent compounds are reduced to the tri- and di-valent state respectively, by electrolysis. Bültemann continued the investigation of the double salts of vanadium, corresponding to the ordinary alums. The preparation of these vanadium alums by electrolysis was based fundamentally on keeping the anode and cathode liquors separated by means of a porous cell. He describes the apparatus used and the various salts prepared. The only one of interest is the vanadium-ammonium alum, $V_2(SO_4)_3(NH_4)_2SO_4.24H_2O$. The anode liquor used was sulphuric acid of the same concentration as the cathode liquor, which consisted of 100 cubic centimeters of a sulphate solution of tetra-valent vanadium. The catholyte was prepared as follows: 25 gm. of acid ammonium metavanadate was dissolved in 31.4 grams of concentrated sulphuric acid, and heated on a water bath with 200 cc. of saturated sulphurous acid until all the vanadium was in solution. This solution then had a blue color, indicating the presence of the tetra-valent compound. This process requires time, and much of the water was evaporated. After cooling, the solution was filtered; the filtrate after being made up to 100 cc. was ready for electrolysis. The anolyte was put into the porous cup and placed in a beaker of convenient size, and the catholyte added. A platinum wire, 0.15 cm. in diameter, served as anode. The cathode was circular in shape, having an area of 160 square centimeters, and was made of lead. Good circulation of the electrolyte was required which was accomplished by introducing a current of hydrogen. Used 8 amperes, that is 0.05 ampere per square centimeter. Duration of experiment was 43 minutes; voltage 8 to 9; temperature 80° C. At the end of the experiment, the catholyte was poured off and allowed to cool in a closed vessel. A large quantity of bluish-violet crystals of vanadium ammonium alum separate out.

Bültemann observed that this alum occurs in two modifications, analogous to chromium aluminium. By treating the ammonium metavanadate with less sulphuric acid than called for above, he obtained after electrolysis a brown solution instead of a green one, as before; and the crystals separating out were of garnet color instead of bluish-violet. These red crystals in acid solution changed to the bluish-violet crystals. The garnet crystals may also be obtained by recrystallizing the bluish-violet ones from an acid solution. The alum is fairly stable, but if the solution is in contact with air it readily oxidizes. ("Zeitschrift für Elektrochemie," **10**, 141-143. Contribution to the knowledge of the electrolytic preparation of tri-valent vanadium salts.) This alum may prove of value in obtaining metallic vanadium from aqueous electrolytes (Fischer).

Eugen Renschler prepared the tri-valent vanadium ammonium sulphate similarly to Bültemann, "Zeitschrift für Elektrochemie," **18**, 137 (1912). The preparation of vanadium salts by electrolysis.

Dr. R. Luther found that chloric acid oxidizes more readily by electrolysis if tri-valent vanadium is present in the electrolyte. With no vanadium present in the acid solution 1.8 volts were required for electrolysis at the start, rapidly decreasing to 0.6 volt; with vanadium present the electromotive force rose to 2.2 volts. When the ClO_3 ion was present there was much less polarization. "Elektrochemische Aktivierungserscheinungen" (The electrochemical activity shown by vanadium compounds), "Zeitschrift für Elektrochemie," **13**, 1907.

Bleecker mentions a method for obtaining vanadic acid electrolytically. Notes on the chemistry and metallurgy of Vanadium: "Metallurgical and Chemical Engineering," **8**, 666-671; and **9**, 209-213, 499-505. The article is divided into three parts: I. The Chemistry; II. Methods of Analysis, and III. The Metallurgy. Sodium vanadate liquor, free from chlorides, is purified by making the solution slightly alkaline with sodium carbonate and heating up to 90° C. The liquor is decanted into an evaporator and concentrated to 30° Baumé, giving a solution which will contain about 200 gm. of vanadic acid per liter, depending upon the amount of sodium vanadate present. Electrolyze in a compartment cell, consisting of a porous cup of 8 liters capacity which contains the vanadium liquor, and a jar holding 5 to 10 gallons (19 to 39 liters), containing a dilute solution of sodium hydroxide. The anode is platinum foil 6 in. x 6 in. (15 cm. x 15 cm.), and the cathode is either iron or copper; preferably the latter. The voltage used depends upon the resistance of the porous cell and is about 6 to 8 volts. The current density will be 30 amperes per square foot (33 amp. per sq. dm.). The sodium ions pass through the porous partition into the cathode compartment, leaving vanadic oxide ions in the anode compartment. Since sodium vanadate is very soluble in water, and vanadic acid practically insoluble, a precipitation occurs on removing the alkali. The presence of mineral acids interferes seriously with the reaction, since vanadium oxide is soluble in dilute acids. If small amounts of chlorine are present in the electrolyte it is partly liberated at the anode, part forms complex vanadyl compounds, giving an impure product. The presence of sulphuric acid causes the precipitation of sodium vanadyl-sulphate containing 73 percent vanadic acid. Any lime or silica not previously removed by filtration will precipitate in part in the anode compartment just as the solution becomes neutral. Some impurities enter the product in spite of the best care taken in the manipulation, probably due to the disintegration of the porous cell.

A patent was granted Bleecker on a process for the electrolytic separation of vanadium and uranium (U. S. Pat. 1,050,796, Jan. 21, 1913). The solution containing these two elements is heated to 90° C., and treated with sodium hydroxide in sufficient quantities to precipitate the uranium. The precipitate thus formed contains some vanadium hydroxide which is recovered by electrolysis as follows: the precipitate is well washed with water and then dissolved with sulphuric acid. The solution is then made slightly alkaline with sodium carbonate and electrolyzed with an anode of iron, nickel, or copper. The vanadium is recovered as vanadium oxide, an anode product, the uranium remaining in solution.

P. Truchot determined vanadium by electrolyzing a hot, slightly ammoniacal sodium vanadate solution. The solution was decomposed, depositing the vanadium as an oxyhydrate on the cathode. The vanadium content of the solution may be from 0.012 to 0.05 gm. vanadic acid per 200 cc. of electrolyte. Temperature of electrolyte, 80° to 90° C. The voltage employed was 2 to 2.25 volts, and the current density was 0.3 amperes per 8 square centimeter cathode surface. The electrolysis lasted 8 to 10 hours. The successful operation requires that the volume of the electrolyte be kept constant by the addition of water from time to time. The water added should contain a little ammonia. The oxyhydrate is precipitated on the cathode as a brown deposit, and when dried and heated gives vanadic acid. "Les Annales: Chimie analytique applique, **7**, 165-167." "Chemisches Zentralblatt," LXXIII, **5**, 1423-1424.

R. E. Myers electrolyzed a sodium vanadate solution acidulated with sulphuric acid, using a mercury cathode. The electrolyte changed from a blue to a green color, but no increase in weight was observed at the cathode. ("Electrochemical Analysis by use of a Mercury Cathode," Journal of the American Chemical Society, **26**, 1130.)

2. *Electrolysis of Aqueous Solutions of Vanadium Salts for Obtaining Metallic Vanadium.* In a statement made by Bleecker

in his article on the Chemistry and Metallurgy of Vanadium, in the Metallurgical and Chemical Engineering, **8**, 666-671, he declares that he has never found vanadium to possess electropositive properties, but that it is always found as an anode product. Truchot, however, claims to have found a cathode product in the form of an oxyhydrate. Sherard-Cowper-Coles, Setterberg and Fischer also obtained vanadium, or some vanadium compound, at the cathode.

In general, it may be said that nearly all of the attempts to obtain metallic vanadium from aqueous solutions by electrolysis have failed, with the exception of the method used by Cowper-Coles, and his work even is doubtful, as several investigators have not been able to repeat his experiments successfully.

L. Schicht in the Chemical News, **41**, 280; and **42**, 331, describes his work on electrolytic vanadium. It is, in brief: vanadium chloride was dissolved in water and hydrochloric acid, and this solution then electrolyzed. No deposition took place in the blue solution, the vanadium compound being merely reduced.

G. Gore, in his book on Electrochemistry, describes attempts to obtain metallic vanadium (pp. 101 to 102). 1. A solution composed of vanadic acid dissolved in pure dilute hydrofluoric acid was electrolyzed with a current obtained from ten Smee elements. Electrodes used were a gas carbon anode and a platinum cathode. A gas having the odor of ozone was liberated at the anode. No vanadium was obtained. 2. A dilute sulphuric acid solution saturated with ammonium vanadate was electrolyzed, using platinum electrodes; a current was supplied from four zinc and platinum elements excited by dilute sulphuric acid. The conductivity of the vanadium solution was very low. During the electrolysis the solution changed gradually to a very intense bluish-black color at the cathode, and a jet black powder of some thickness was deposited on it.

C. Setterberg did not obtain metallic vanadium on electrolyzing a solution containing a vanadium salt. On electrolyzing a solution of ammonium meta-vanadate he obtained a dark red precipitate of vanadic acid at the anode. Ammonia was liberated at the cathode. Furthermore, he subjected a concentrated solution of V_2O_4 dissolved in hydrochloric acid to electrolysis, using a porous cell. The blue solution in the porous cell became dark brown in color very rapidly, and a black, brittle deposit was obtained on the cathode. The compound in all probability was the sesquioxide of vanadium. Vanadic acid was deposited on the anode. Solutions of vanadyl chloride and tetrachloride showed such low conductivity that they could not be used. (Gmelin and Kraut: "Handbuch für anorganische Chemie," Vol. III_2, p. 64.)

Sherard-Cowper-Coles claims to have succeeded in electrolytically depositing metallic vanadium as follows: The electrolyte was prepared by boiling vanadic acid with an excess of sodium hydroxide and decomposing the vanadate thus formed with an excess of hydrochloric acid. In detail: Dissolve 1.75 parts of vanadic acid (V_2O_5) and two parts of sodium hydroxide in 160 parts of water; to this clean solution add 32 parts of hydrochloric acid. The solution thus formed will contain one ounce of vanadic acid per gallon (106 gm. per liter). Current density used was 18 to 20 amperes per square foot (2.0 to 2.2 amp. per sq. dm.); the voltage was 1.88 volts between the terminals. The electrolysis was conducted at a temperature of 180° F. (82° C.). Experiments were performed, using a higher and a lower current density, but the results were unsatisfactory, as the metal at the cathode was contaminated with red oxide. It was found that the temperature also has an important rôle, as it causes an impure cathode product if it is below 180° F. (82° C.). Under the conditions described above, silvery metallic vanadium having very high metallic luster was deposited and adhered tightly to the cathode. The solution when first made is greenish-yellow in color. After boiling with a carbon anode it becomes darker, and on passing the current is changed to a dark green. When much metal was deposited out, the color changed to a bluish tint. When two ounces of vanadic acid per gallon (212 gm. per liter) were used, the deposited metal, instead of being a silvery white, was grayish in color. ("Institution of Mining and Metallurgy," 1898 and 1899, pp. 198 to 200; and "Chemical News," 1899, p. 147. "Notes on the Electrodeposition of Vanadium.")

Great hope was expressed, in the Spanish journal *Revista Minera,* in the development of the Cowper-Coles process, as Spain at that time had the richest known vanadium deposits; but the process never became commercial. ("Zeitschrift für Elektrochemie," **6**, 171, 1899 to 1900.) Borcher and McMillan claim that they never succeeded in repeating Cowper-Coles' experiments. ("Electric Smelting and Refining," pp. 489 to 490.)

Gustav Gin states that, on repeating the work of Cowper-Coles, he observed that the metallic deposit soon stops, tarnishes and does not exceed a very limited thickness. According to Gin, it seems that the deposit is at first protected by a film of hydrogen, which soon loses its efficacy. Gin believes that at the present time (1909) it is impossible to produce metallic vanadium commercially from aqueous solutions by means of the electric current. (Trans. Amer. Electrochem. Soc., **16**, 439-441.)

The object of this thesis is to determine if it is possible to deposit metallic vanadium from aqueous salt solutions by means of the electric current This question has never been satisfactorily answered, and the amount of work done along this line does not permit of a definite conclusion.

In the introduction is given an outline of the work done up to date. The only reference found, which gives conditions whereby metallic vanadium was obtained is that of Sherard-Cowper-Coles: "Notes on the Electrodeposition of Vanadium," published in the "Institution of Mining and Metallurgy," 1898 and 1899, pp. 198 to 200. This, then, is the natural starting point and, while the electrolyte should come rather under the head of mixed salts, the investigation was undertaken for the purpose of improving the Cowper-Coles method, if possible, and making the process a commercial one.

EXPERIMENTAL WORK.—PART I.

Investigation of Sherard Cowper-Coles' Work. In his treatise on the subject, Cowper-Coles gives the conditions under which he claimed to have obtained the metal. He also describes the deposit obtained. The electrolyte which he used consisted of 1.75 parts vanadic acid (V_2O_5); 2.00 parts sodium hydroxide, and 160.00 parts water. This mixture was then boiled, and 32 parts of hydrochloric acid added.

He studied various current densities and changes in temperature, and claimed the best results for the following conditions: 18 to 20 amperes per square foot (2.0 to 2.2 amp. per sq. dm.) cathode surface (0.125 to 0.139 amperes per square inch); voltage, 1.88 volts; temperature, 180° F. (82.2° C.). Under these conditions it was claimed that the vanadium obtained was very dense and its color that of silver.

In order to get the proper conditions for depositing metallic vanadium, a series of 55 experiments was made, starting with the conditions given by Cowper-Coles; and then changes were made in current density, in temperature, in cathodes, and in concentration. The effect of addition agents was investigated, and the action of the electric current on the neutralized electrolyte of Cowper-Coles was studied. Tests also were made, using a porous partition to keep the catholyte and anolyte separated. The results are tabulated in Table I.

Summary and Conclusions.

1. Metallic vanadium cannot be obtained by electrolyzing the Cowper-Coles electrolyte.
2. The reduction of the electrolyte is limited in most cases to the vanadyl state, which is blue (V_2O_4).
3. With the exception of experiments 12 to 15, and 40 to 43, all tests show a reduction of the electrolyte.
4. With high temperatures (90° C. or over) the reduction can go to the V_2O_2 state, lavender color.
5. Lead electrodes alone give a reduction to the sesquioxide or green state (V_2O_3) at temperatures below 90° C. Above 90° C. the electrolyte is reduced to the lavender state (V_2O_2).
6. Carbon electrodes reduce the electrolyte to the sesquioxide form (V_2O_3), green color.
7. Platinum cathodes at temperatures below 90° C. reduce the electrolyte to the blue vanadyl state only (V_2O_4), and the current density seemingly has no further effect. At temperatures of 90° C. and above the lavender state (V_2O_2) is reached only when porous cells are used; otherwise not.
8. The black deposit on platinum cathodes is not a vanadium compound.

From these 55 experiments, it is clear that metallic vanadium cannot be obtained from Cowper-Coles electrolyte under the most favorable conditions, in regard to the reducing action at the cathode; the variation of conditions, such as electrodes, temperature, current density, concentration, and separation of anolyte and catholyte. It is therefore obvious that the results obtained by Sherard-Cowper-Coles are erroneous, as well as the statement of Gustav Gin that he obtained metallic vanadium by Cowper-Coles method. (Transactions of the American Electrochemical Society, **16**, 439.)

Both authors evidently mistook platinum hydride, which may vary in color from light gray to black, for vanadium. By testing the conductivity of the cathode deposit, and by ignition in the flame of a Bunsen burner, it was proven in later experiments, in which the same deposit occurred, that it was platinum hydride. The measurement of the resistance between equal distances over the surface of the platinum cathode, by means of a millivolt potentiometer, *i. e.*, the voltage drop between the ends of two wires, one centimeter apart, was 11 millivolts at all points on the surface of the cathode. As the film was very thin, not much stress can be put on the conductivity test.

Experiments Nos. 10 and 53 were repeated, being run for two hours and ten minutes each; the electrodes were tested in the manner described above. The results were as follows: The cathode of No. 10 at the start weighed 5.8006 grams, and after electrolysis 5.8008 grams. The increase in weight was 0.0002 gram. After ignition the weight of the cathode was identical in appearance with that of the original electrode.

The cathode of No. 53 at the start weighed 5.8006 grams. After the electrolysis the weight was between 5.8007 and 5.8008 grams. After igniting, the weight of the cathode was 5.8006. In both cases the electrodes after ignition were perfectly bright, showing no indications that there had been any deposition. These tests prove clearly that the deposits obtained were platinum hydride, and not metallic vanadium.

EXPERIMENTAL WORK—PART II.

Electrolysis of Solutions of Mixed Salts. A series of 112 experiments were performed on electrolytes containing another salt besides the vanadium compound. The method of J. Koppe and E. C. Behrendt for the preparation of double salts was tried. This method for producing the double sulphate consists in dissolving metavanadic oxide in an excess of dilute sulphuric acid, and reducing the solution with sulphur dioxide gas. To this reduced solution is added an excess of the sulphate with which the vanadium is to form the double salt, and the solution then carefully evaporated first on the water bath, and finally at a higher temperature. A voluminous deposit is obtained, light blue in color. The mother liquor is poured off, and powdery blue mass put into a large volume of water. The double salts of vanadium are not very soluble, so settle out, and may be easily filtered. The following double sulphates of vanadium were prepared: ammonium, calcium, magnesium and aluminium, but as they were found not to be very soluble, their solutions were valueless as electrolytes. (J. Koppe and E. C. Behrendt: "Zeitschrift für anorganische Chemie," **35**, 154-186.)

As the double salt solution of vanadium could not be used for electrolytes, other means had to be employed to study the effects of various inorganic salts on the electrolysis of vanadium compounds. This was accomplished by adding the salts in question to a solution of some vanadic salt such as the sulphate, fluoride, etc. The results are tabulated in Tables II to VI.

Summary of Conclusions. In a majority of the tests made a black film was formed on the cathode wherever platinum was used. This coating, on careful washing, gave no indication of the presence of vanadium.

Carbon anodes, when used in connection with mercury cathodes, or with the vanadium fluoborate or fluosilicate disintegrate.

Monel metal cathodes are unsatisfactory, in that they are readily attacked by the electrolytes, the nickel being attacked and the copper remaining in a finely divided form. These electrodes show a decrease in weight after the electrolysis.

In Experiments Nos. 87 and 88, Table IV, where a porous cup was used, a definite cathode deposit formed. The catholyte was a solution of the mixed vanadic (V_2O_5) sulphate, and magnesium sulphate. The deposit was grayish-brown, and non-homogeneous, composed of brown and white particles. The analysis of the deposit is 24.88 percent metallic magnesium and 25.46 percent vanadic oxide (V_2O_5). The formation of this deposit was slow, only 0.6875 gram being formed during the run of four hours.

The electrolyte of the mixed vanadic and ammonium sulphate is ordinarily reduced to the blue vanadyl state (V_2O_4). When boric acid (B_2O_3) is added to saturation, the reduction at the cathode continued to the green sesquioxide form (V_2O_3).

Electrolytes containing the mixed vanadic and aluminium sulphates are generally reduced to the green sesquioxide state (V_2O_3). With a high current density (0.76 to 2.01 amperes per sq. in. or 0.12 to 0.31 amp. per sq. cm.), the electrolyte used as catholyte in a porous cell, with a platinum cathode, was reduced to the lavender state, corresponding to the oxide V_2O_2 or VO. This phenomenon is independent of the temperature.

The mixed vanadic and magnesium sulphate electrolytes were generally reduced to the blue vanadyl state (V_2O_4) if a low current density was employed. The reduction proceeds to the green sesquioxide form (V_2O_3) by high current densities at cathode. This occurs whether a porous cup is used or not, and the intensity of the reduction increases with the rise in temperature.

Vanadium fluoborate and vanadium fluosilicate electrolytes are limited in their state of reduction to the blue vanadyl form (V_2O_4). The original green or yellowish-green of both these electrolytes is due to a partial reduction from the yellow vanadic to the blue vanadyl form, both mixing and giving a green color to the original electrolyte. This green color must not be mistaken for the sesquioxide green color.

The sesquioxide state of vanadium electrolytes can only be reached by first passing through blue vanadyl state (V_2O_4). This fact may be readily observed in the course of electrolysis experiments, Nos. 47 and 48, Table III.

EXPERIMENTAL WORK—PART III.

Salts with Acids. The incentive to this thesis was originally given by a series of approximately one hundred experiments on acid electrolytes containing vanadium, which were performed at the Colorado School of Mines and Lehigh University during the years 1910 to 1915. The idea was to devise a hydro-electrolytic method for obtaining vanadium from carnotite concentrates, and concentrates from vanadic sandstones. All the tests made were negative, in so far as obtaining a deposit of vanadium by electrolysis was concerned. The electrolytes employed were acid solutions, obtained by leaching the concentrates extracted from carnotite and vanadiferous sand-stones with dilute solutions of different acids. The concentrates were collected by a process of attrition and the separation of the vanadium mineral from the gangue by flotation (S. Fischer: "The concentration of carnotite ores and some similar ores," Met. and Chem. Eng., **10**, 356 to 359 (1912).

Only one set of tests is of interest; the tests for which dilute nitric acid was employed as the leaching agent. The electrolyte used was prepared as follows: 10 grams of carnotite concentrates, containing 12 percent V_2O_5, was leached with 10 c.c. of concentrated nitric acid made up to 100 c.c. with water. A dark green solution was obtained, having specific gravity of 1.10 at 32° C. This solution, upon being electrolyzed, turned yellow, and the specific gravity was reduced during electrolysis from 1.08 to 1.06. Under these conditions, at a temperature between 20.1° and 25° C., a yellowish-brown precipitate separated from the solution, which proved to be a hydrated oxide of vanadic acid. On testing the solution for vanadium, not a trace could be found.

In the following 123 experiments, both organic and inorganic acids were used to form salts with vanadic acid, and the solutions subjected to electrolysis, varying current density, temperature, concentration and electrodes, both with and without the use of a porous partition. See Tables VII to XII, inclusive.

Conclusions. After investigating a number of inorganic and organic acids as solvents for vanadic acid, it may be said that none act satisfactorily as electrolytes for obtaining electrode deposits. The reduction at the cathode was insufficient to reduce the salt to the metallic form.

Vanadic acid, dissolved in dilute hydrochloric acid, gives a greenish-yellow solution which on electrolysis passes from this green color, through the blue vanadyl state (V_2O_4) to the green sesquioxide state (V_2O_3). If a platinum cathode is employed, a gray to black film is formed, varying in amount and tendency towards a black color, directly as the time and the current density. This deposit contains no vanadium, it being a coating of platinum hydride.

If dilute sulphuric acid is employed as solvent for vanadic oxide (V_2O_5) a yellow solution is obtained. This on electrolysis is reduced to the blue vanadyl state (V_2O_4) giving no deposit containing vanadium on either cathode or anode.

Dilute nitric acid only dissolves very little vanadic oxide (V_2O_5) (less than 0.5 gram V_2O_5 per 100 c.c. of dilute acid). The amount of vanadic oxide dissolved varies only slightly with the concentration of the nitric acid. The concentrations employed were: 1 to 1, 1 to 2, 1 to 3, 1 to 4, and 1 to 5 parts by volume of concentrated nitric acid to parts water. In no case was more than 0.5 gram of vanadic acid dissolved in 100 c.c. of the solvent.

A dilute hydrofluoric acid solution of vanadic oxide has a yellowish-green color. On electrolyzing the solution is reduced to the vanadyl state (V_2O_4). No deposition takes place when a platinum cathode is employed. A monel metal cathode was partially attacked, nickel going into solution, leaving non-adherent particles of copper, similarly as in Experiments Nos. 34, 44 to 47, Part I.

Vanadic oxide dissolved in a dilute solution of lactic acid gives the blue vanadyl color, which does not show any further reduction on electrolysis. This original blue coloration is evidently due to the organic acid used, reducing the vanadic acid and forming the vanadyl lactate. Where no porous partition was employed to keep the anolyte and the catholyte separate, a black film of platinum hydride formed on the platinum cathode, the catholyte being the vanadyl lactate solution. On using a porous partition, a brown, very thin coating was formed on the platinum cathode, which on ignition gave forth an organic odor. The globular residue left after ignition dissolved with a yellow color in sulphuric acid and gave a test for vanadium. The residue was fused vanadic acid.

A solution of vanadic oxide in dilute ethyl sulphuric ($C_2H_5.HSO_4$) acid, has a light green color which, on electrolysis, changes to the blue vanadyl state (V_2O_4). No deposit is formed on the platinum cathode, whether a porous cup is used or not.

Vanadic oxide dissolves, giving a blue colored solution (in dilute tartaric acid), the intensity of the blue color depending on the amount of vanadic oxide dissolved. No change in the color of the electrolyte was noticed in eighteen experiments made with varying concentrations from 0.014 to 0.448 gram of vanadic acid per c.c. Neither the current density variations, 40 to 161 amperes per sq. ft. (4.4 to 18 amp. per sq. dm.) nor the temperature changes (20° C. to 98° C.) had any further reducing effect on the electrolyte. Also, under these same conditions, no deposit of vanadium formed on either the anodes or the cathodes.

On using concentrated acids as solvents for vanadic oxide, it was observed that the amount of vanadic oxide dissolved in the different concentrated oxides was not the same. Concentrated hydrochloric acid (sp. gr. 1.18 to 1.19) dissolved 0.133 gram vanadic acid per c.c. Concentrated sulphuric acid (sp. gr. 1.84) dissolved 0.02 to 0.304 gram vanadic oxide per c.c., depending on the purity of the vanadic oxide used, or the temperature of the solvent, and on the amount of water absorbed by the sulphuric acid. A very small amount of moisture in the concentrated sulphuric acid causes a rapid increase in the mount of vanadic oxide dissolved. Concentrated nitric acid (sp. gr. 1.42 to 1.425) practically dissolves no vanadic oxide when cold, and only very little when hot, much less than 0.0025 gram of vanadic oxide being dissolved in 1 c.c. of the hot concentrated nitric acid. Vanadic oxide dissolves to the extent of 0.81 gram per c.c. in concentrated lactic acid (sp. gr. 1.21) when hot. On cooling, a voluminous precipitate separates from the solution which, on ignition, emits an organic odor. On slowly heating, an odor peculiar to lactic acid is given off, indicating that the compound is evidently the vanadyl lactate.

In electrolyzing a solution of concentrated hydrochloric acid saturated with vanadic acid, a reduction of the electrolyte occurs, ranging from an originally greenish-blue, through blue to the green sesquioxide state (V_2O_3). When a platinum cathode is used a gray to black film is formed, showing no vanadium. This cathode deposit was found to be platinum hydride. If a carbon anode and a platinum cathode are employed a — E. M. F. of 0.025 volt is obtained. On the other hand, using a lead and a carbon electrode a + E. M. F. of 0.1 volt, indicates that the lead in this case acts as anode.

The electrolysis of concentrated sulphuric acid (sp. gr. 1.84) saturated with vanadic oxide, gives a green salt deposit on the cathode. In all the literature on vanadium up to date no indication could be found that this had been done. Brierley, in 1886, electrolyzed a solution containing vanadyl oxide (V_2O_4) in dilute sulphuric acid, using it as the catholyte in a porous cup. He obtained the sesquioxide solution, green in color, corresponding to the salts of the oxide (V_2O_3). This green solution was then treated with strong sulphuric acid of twice its volume. After standing for twenty-four hours a green precipitate separated, having the formula "$V_2O_3(SO_3)_4.9H_2O$," according to Brierley. In the same paper mention was made of the fact that this salt could not be isolated, due to its being so readily oxidized. It is, therefore, rather difficult to say whether the formula given by Brierley is an assumption, or whether the product was actually analyzed. Brierly, J. Chem. Soc., **49**, 822 to 824 (1886).

It was found that, under no condition was it possible to determine the composition of the green sulphate salt, as this compound was very soluble in the water or the alcohol required for washing. The wash solution in each case showed the blue vanadyl color (V_2O_4). Even ether dissolved some of the green sulphate salt as soon as it mixed with the concentrated sulphuric acid adhering to the small crystals of the deposit.

Attempts were made to obtain the green sulphate deposit on the cathode. It was freed from the adhering acid as well as possible by washing very quickly with water. The salt was then dissolved in water and recrystallized. As soon as water was used, the salt was oxidized to the blue vanadyl state, and the analysis was then made on this product. In alcohol the green deposit also dissolved, giving a blue colored solution. The analysis of the blue salt obtained after recrystallizing from the aqueous solution and drying at 100° C. gave the following analysis: 42.54 percent V_2O_4 and 43.83 percent SO_3. This composition did not coincide with the composition of any of the sulphates in the literature, and the blue salt was dissolved and recrystallized four times and the product again analyzed, and found to contain 42.56 percent V_2O_4 and 40.49 percent SO_3.

It was found that the vanadium content in both instances checked. The SO_3 content in the second case, however, was lower. This was evidently due to the fact that in the first case not all free sulphuric acid had been eliminated by washing. On comparing these results with the vanadyl sulphates known it was found that the ratio of V_2O_4 to SO_3 equals 1 to 0.953 for the salt $VOSO_4.2H_2O$. The same ratio in the second analysis is V_2O_4 to SO_3, equals 1 to 0.952. This was evidently the salt formed, the difference in percentages being due to partial elimination of the water of crystallization.

In other ways the recrystallized blue sulphate salt behaved like the compound $VOSO_4.2H_2O$. For instance, on evaporating an alcoholic solution containing the salt, the blue crust left swells, giving the whole a blistered appearance. The crust after grinding was not readily soluble in cold water, but remained suspended like powdered aluminium. The blue powder formed from the blistered crust obtained from the alcoholic solution after evaporation, is made up of small plates (microscopic) and in moist air deliquesces to a thick blue syrup. It may be concluded, therefore, that the salt obtained by electrolysis is a sesqui-vanadium-sulphate, which on dissolving in water gives the vanadyl sulphate $VOSO_4.2H_2O$ on evaporation.

A hot concentrated solution of lactic acid, saturated with vanadic oxide, has so low an ionization that the electric current does not pass, even on putting the cell directly across the terminals of 120 volt D. C. source.

Regarding the electrodes, it may be said that carbon anodes in concentrated sulphuric acid electrolytes disintegrate, and that lead anodes become coated with a film of sulphate, thus increasing the resistance to such an extent as to make the passage of the electric current difficult. Lead cathodes in concentrated and dilute hydrochloric acid electrolytes tend to become coated with lead chloride, which was observed in every instance where such electrodes were used in this solution. The lead chloride, being very insoluble, collected at the bottom of the receptacle.

It was ascertained in the course of these investigations that the black deposit, which formed on the platinum cathodes, was platinum hydride which, under certain conditions, such as low current densities and the short duration of time for the passage of the electric current, will give a light gray coating, metallic in appearance which, if not carefully investigated, might be taken for a deposit, such as metallic vanadium. Upon increasing the length of time for the passage of the current, such deposits increase somewhat in thickness, giving the deposit a dark gray to black color. The color and thickness of the coating is also directly proportional to the current density, it increasing as the current density is increased.

EXPERIMENTAL WORK—PART IV.

As vanadium in many respects resembles antimony and arsenic, it was thought likely that it would be deposited from a similar electrolyte. (Table XIII).

Conclusions. Vanadium cannot be deposited from an alkaline sulphide electrolyte, such as is used in the electro-deposition of antimony.

EXPERIMENTAL WORK—PART V.

The Alkali Vanadate Electrolytes and the Anode Reaction. Vanadium forms a large number of acids, of which the most important ones are the ortho (H_3VO_4), the meta (HVO_3) and the pyro ($H_4V_2O_7$) vanadic acids. In addition to these, vanadium forms polyacids. The series of salts formed from the various types of vanadic acids exceeds those of any other inorganic element. In forming ortho, meta and pyro acids, vanadium resembles silicon, phosphorus and arsenic.

The vanadic acid (V_2O_5) of commerce is the anhydride of metavanadic acid HVO_3. ($2HVO_3 = H_2O + V_2O_5$).

Vanadic acid occurs in three modifications: the two yellow and red amorphous forms, and the gray crystalline form. The yellow amorphous form is a powder, golden to orange yellow in color. It is partly soluble in water, one liter of water dissolving approximately 300 milligrams. The red modification is amorphous and brick-red in color. It is slightly more soluble in water than the yellow form, its maximum solubility being about 500 milligrams per liter. The crystalline form is obtained by fusing either of the amorphous modifications, giving a dark gray, brittle crystalline mass. This mass, when finely ground, is dark red in color. In the melted form, the crystalline vanadic acid acts readily on the container in which it is fused, attacking even platinum. Fused in silica ware, it forms silicates; and when fused in carbon containers it forms carbides. The three modifications dissolve in dilute hydrochloric and dilute sulphuric acid. The sulphate solution is yellow colored, and the hydrochloric acid solution is yellow to yellowish-green. Dilute nitric acid has little solving effect on vanadic acid. In water the amorphous modifications give a yellow solution. Vanadic acid dissolved in concentrated hydrochloric acid gives a dark bluish-green solution; dissolved in concentrated sulphuric acid a brownish-yellow solution is obtained. Concerning the alkali-hydrates, vanadic acid is most readily soluble in sodium hydrate; to a lesser degree in potassium hydrate, and very difficultly soluble in ammonium hydrate. One of the best solvents of vanadic acid is a solution of sodium peroxide containing hydrogen peroxide. A very good summary on the chemistry of vanadium and its salts is given by Warren F. Bleecker, in his article "Notes on the Chemistry and the Metallurgy of Vanadium," Part I. (Met. and Chem. Eng., **8**, 666-671 (1910)).

Of the many possible alkali vanadates, only one form is of importance, the metavanadates. The ortho, pyro and the intermediate vanadates very readily transform into the stable meta modification, liberating alkali at the same time.

A series of 33 experiments was run on the sodium metavanadate, in order to study the effects produced at the cathode, the anode and in the electrolyte. The sodium metavanadate used in these tests was obtained from Merck and Company, and was chemically pure.

In experiments Nos. 1, 2 and 3 an electrolyte containing 0.007 gram of sodium vanadate ($NaVO_3$) per c.c. was electrolyzed between a platinum cathode and a carbon anode. The anode current density varied between 12 to 19 amperes per sq. ft. (1.3 to 2.1 amp. per sq. dm.) and the temperature ranged from 20° C. to 74° C. The platinum cathode showed a dark film, giving no test for vanadium: it was platinum hydride. The increase in weight of the cathode due to this black film was 0.0003 gram. On ignition of the cathode in the flame of a Bunsen burner and reweighing, it was found that the cathode weighed the same as at the start of the experiment. The anode gave indication of a slight deposit, reddish in color, which dissolved in the course of electrolysis, giving the electrolyte an orange yellow color.

The same electrolyte was used for experiments Nos. 4 to 7, but instead of using a carbon cathode, a platinum wire was employed, and boric acid was added to the solution to saturation. The anode current density ranged from 33 to 164 amperes per sq. ft. (3.6 to 18 amp. per sq. dm.), and the temperature ranged from 18° to 113° C. The results obtained coincided with those for tests Nos. 1, 2 and 3.

In experiments Nos. 8, 9 and 10 the electrolyte was of the same concentration as in experiments Nos. 1, 2 and 3, but saturated with boric acid. The anode current density corresponded to that used in those experiments, but the temperature was only permitted to rise to 69° C. The results obtained corresponded in every detail to those in experiments Nos. 1 to 7.

The electrolyte of experiments Nos. 11 to 17 contained 0.007 gram of sodium metavanadate per c.c. to which was added approximately 0.0001 gram of an addition agent. The agents used were glue, quinoline and tannic acid. The current density varied from 24 to 115 amperes per sq. ft. (2.6 to 13 amp. per sq. dm.). The temperature range was from 25° to 99° C. Both electrodes were of platinum, the cathode being a No. 18 B. & S., so as to promote the oxidizing action at the anode. The anode showed a slight red deposit of vanadic oxide. Platinum hydride formed on the wire cathode. The electrolyte changed from a colorless to an orange yellow solution, the color change starting at the anode.

In experiments Nos. 18 to 21 the electrolyte contained 0.007 gram of sodium metavanadate per c.c. and was saturated with boric acid. Glue and quinoline were tried as addition agents, being added to the extent of 0.0001 gram per c.c. of electrolyte. The results obtained in these tests were identical with those of experiments Nos. 11, 12, 13 and 14, the presence of these organic addition agents having no effect upon the results of the electrolysis.

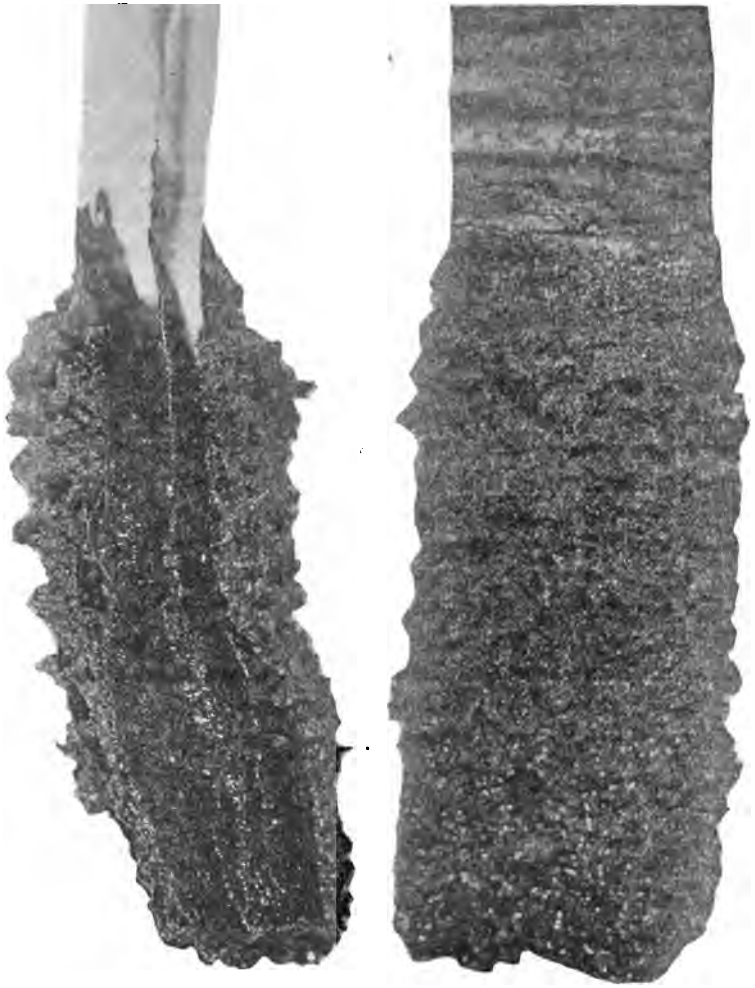
Experiments Nos. 22 to 33 involved a change in concentration of the electrolyte. In Nos. 22 to 25, the electrolyte contained 0.143 gram of sodium metavanadate per c.c.; Nos. 26 to 29 the concentration was 0.076 gram per c.c., and in Nos. 30 to 33 the concentration was 0.036 gram per c.c. The anode current density used in each case was from 24 to 196 amperes per sq. ft. (2.6 to 21.6 amp. per sq. dm.). The temperature ranged from 18° to 97° C. The electrodes were a carbon anode and a platinum

cathode. As in the previous experiments, the colorless electrolyte changed to orange red, starting at the anode. The red deposit on the anode seemed to remain only after the electrolyte had been completely changed to the yellow state. Platinum hydride formed on the cathode.

In an article published by Warren F. Bleecker entitled, "Notes on the Chemistry and Metallurgy of Vanadium," the author gives a brief outline of an electrolytic method for obtaining vanadic oxide. He used a porous cup in which the anolyte was contained. The anolyte is a solution of sodium metavanadate in water. Its concentration was 0.2 gram vanadic oxide (V_2O_5) per c.c. The catholyte was water containing a small amount of sodium hydroxide. The anode was platinum and the cathode iron or copper. The anode current density used was 30 amperes per sq. ft. (3.3 amp. per sq. dm.) at the anode. Bleecker states that "without taking more than the usual precautions, the grade of the anode product should be 98 percent V_2O_5, the impurities being principally lime and silica." Bleecker: "Notes on the Chemistry and Metallurgy of Vanadium," Part III. (Met. and Chem. Eng., **9**, 503-504 (1911)).

Bleecker not only deserves all the credit for having done the most valuable work in the recent development of the metallurgy of vanadium, but he also was the first to devise the electrolytic method for obtaining vanadic oxide on a commercial basis from sodium metavanadate electrolytes. It is only to be regretted that Bleecker did not give more detailed information concerning the reactions taking place during electrolysis, and the efficiency of his process. It was therefore thought of value to investigate the reactions taking place in the course of electrolysis of metavanadate solutions and to study the efficiency of the process.

An endeavor was made to prepare a sodium metavanadate electrolyte according to the equation $V_2O_5 + 2NaOH = 2NaVO_3 + H_2O$ by digesting 20 grams of pure vanadic oxide in 100 c.c. solution of 8.79 grams sodium hydroxide. The vanadic oxide (V_2O_5) used was 99.93 percent V_2O_5, and the sodium hydroxide was 98 percent pure. In order to obtain an electrolyte which would contain 0.2 gram of vanadic oxide per c.c. it required therefore 20.02 grams of vanadic oxide (99.93 percent pure) and 8.97 grams sodium hydroxide (98 percent pure). It was found, however, that this amount of sodium hydrate was not sufficient to dissolve the vanadic oxide. At first some of the oxide went into solution; then further additions were simply changed to the grayish-green vanadium hydroxide, and when the last of the vanadic oxide was added, a large bulk of the vanadium hydroxide remained undissolved. Enough sodium hydroxide was then added to give a clear



a FIG. 1. b

solution. It required 22.72 grams of sodium hydroxide (98 percent pure) in 100 c.c. of water to dissolve 20.02 grams vanadic oxide giving a clear solution at 70° C.

Electrolytes of this composition (0.2 gram of vanadic oxide and 0.2 gram of sodium hydroxide per c.c.) were then used in experiments Nos. 34 to 40. The electrolyte was strongly alkaline and had a faint yellow appearance.

In experiments Nos. 34, 35 and 36 a porous cup was used as diaphragm. The anolyte was the metavanadate solution, as described above, while the catholyte was water containing approximately 0.01 gram of sodium hydroxide per c.c. The anode was platinum and the cathode carbon. The anode current density was 15 amperes per sq. ft. (1.7 amp. per sq. dm.). The temperature varied from 18° to 93° C. In test No. 34, the anolyte was practically colorless at the start, but slowly changed in color through faint yellow to lemon yellow, and after two hours and eighteen minutes was dark orange. A thin, brick-red layer of hydrated vanadic oxide formed on the anode, which on drying at 110° C. weighed 0.1253 gram. On fusing this deposit on the platinum anode, it lost 0.0073 gram, giving the crystalline form of vanadic oxide, which weighed 0.1180 gram. The deposit before and after fusion was hygroscopic, but to a much greater extent before fusion had taken place.

The electrolyte left from experiment No. 34 was used as anolyte in a porous cup in experiment No. 35. The anode current density was the same as in No. 34, and the temperature ranged from 66° to 68° C. The anolyte was orange yellow at the start, and remained so during electrolysis. The deposit on the anode was brick-red in color and adhered to the anode in layers (see Fig. 1a). The deposit weighed 2.7938 grams after drying at 110° C., and 2.727 grams after ignition. The test ran for 4 hours and 13 minutes.

Experiment No. 36. A fresh portion of the same electrolyte as was used in experiment No. 34 was neutralized with boric acid and used as anolyte for experiment No. 36. The anode current density employed was 15 amperes per sq. ft. (1.7 amp. per sq. dm.). The temperature ranged from 83° to 93° C A porous cup was used as a diaphragm to separate anolyte and catholyte. The electrolysis lasted for six hours and forty minutes. At the start of the test the anolyte was lemon yellow in color, due to the neutralization of the colorless sodium metavanadate solution with boric acid. After one hour and thirty minutes the anolyte was orange yellow in color. The weight of the anode deposit was 7.058 grams unignited and 6.3647 grams upon ignition.

As the anode ampere efficiency is considered in all of the previous and the following experiments, its theory is most conveniently treated in this place. According to Düllberg the metavanadate of sodium in solution is present as three combined molecules of sodium metavanadate ($NaVO_3$), corresponding to $Na_3V_3O_9$. He determined this fact by conductivity tests and by ascertaining the neutralization curves. Düllberg: "Concerning the Behavior of Vanadates in Solution." (Z. für phys. Chem., **45**, 129 and 182.

The reaction taking place during electrolysis of the sodium vanadate is in all probability as follows: $2Na_3V_3O_9 = 3(V_2O_5 + O) + 6Na$ followed by the secondary cathode reaction $6Na + 6H_2O = 6NaOH + 3H_2$.

During the electrolysis of a sodium metavanadate electrolytes, when using porous cup partitions hydrated vanadic oxide ($V_2O_5.xH_2O$) and oxygen formed at the anode, and hydrogen was liberated at the cathode with an increase in alkalinity of the catholyte. Düllberg does not explain the reactions in the electrolysis, confining himself only to the state in which sodium metavanadate exists in solution. The reaction in electrolysis is evidently first a polymerization of the simple $NaVO_3$ molecules to the molecule $Na_3V_3O_9$, and then the splitting up of this complex molecule into sodium and vanadic oxide plus oxygen. The sodium then combines with the hydroxyl radical (OH) obtained from the decomposed water, giving sodium hydroxide in solution, while the hydrogen is liberated at the cathode.

The question now arises, what is the valency of the vanadic oxide in this connection: two molecules of the polymerized sodium metavanadate may be written in two ways: $2Na_3V_3O_9$, or $Na_6V_6O_{18}$. This latter formula may be simplified by dividing through by 3, giving the formula $Na_2(V_2O_6)$. The radical V_2O_6 is undoubtedly the one appearing at the anode, but is further split up into $V_2O_5 + \frac{1}{2}O_2$. The radical V_2O_6 is di-valent, therefore in calculations of the anode efficiency in the precipitation of sodium metavanadate solutions V_2O_5 may be considered di-valent.

As regards the anode deposit itself, it is best to base the ampere efficiency calculations on the ignited product, as it is very difficult to rid the original product from the accompanying water, giving a very uniform product upon which to base calculations. The unignited product is very hygroscopic, absorbing moisture so rapidly that weighing it is difficult. On heating the original deposit in a beaker immersed in nearly boiling concentrated sulphuric acid for ten hours, and then weighing in a closed receptacle, such as a weighing bottle, it was found that the loss in weight was practically identical with the loss obtained on fusing the deposit. For this reason it was determined to base the efficiency calculations on the weight of the fused product. It may be stated here that the loss in weight on ignition varied between 5 and 10 percent, practically the same figures holding true for the material dried at approximately 300° C. for a long time. This variation in percentage loss in weight is due to the hygroscopic property of the deposit itself, which causes a variation in the original weight of the substance taken for analysis, not every sample of the various anode products contained the same amount of water after drying at 110° C. Most of the anode products were analyzed. The greatest variation was again shown by the product dried at 110° C. On analysis of a large number of samples of the original anode deposit, it was observed that the vanadic oxide (V_2O_5) content varied between 83.33 percent and 90.11 percent. If it is considered that $V_2O_5.H_2O$ contains 91 percent vanadic oxide and knowing that the product is hygroscopic, one is quite justified in assuming the original deposit to be of the type $V_2O_5.\times H_2O$.

The results obtained on the original product when heated at approximately 300° C. for a long time, and on the fused product, checked very closely. The percentage of vanadic oxide content varied between 97.76 and 93.37 percent. A higher vanadic oxide content of either dried or fused product was never obtained in the course of the investigation. The product was always slightly contaminated with lime and silica from the porous cup, especially so if a part of the deposit dropped to the bottom of the cup, which very frequently was the case. It was regularly observed that, after running a test, the inside of the porous cup had been attacked, becoming slimy, and a fine white material collecting at the bottom of the cup. This proved to be silicate of lime.

The ampere efficiency calculation is made according to Faraday's Law.

$\frac{\text{Molecular weight}}{\text{Valency}} \times 0.00001035 \times$ number of coulombs. This gives the theoretical amount deposited in a certain time. Therefore

$\frac{\text{Weight of product found}}{\text{Theoretical weight}} \times 100 =$ percent ampere efficiency.

In this instance the product chosen as a basis of calculation is the one of 98.4 percent purity, because it is unlikely that on any further refinement of the process, such as non-attackable porous cups, a less pure product would be obtained. Taking experiment No. 48, for example, the ampere efficiency figures out as follows:

$\frac{182}{2} \times 0.00001035 \times 0.625 \times 15780 = 9.2896$ grams—therefore the anode ampere efficiency $= (9.1223 \div 9.2896) \times 100 = 96.63$ percent. For all the other experiments a similar calculation will give the corresponding efficiency, so that one calculation will suffice to show the mode of procedure.

The anode ampere efficiencies of experiments Nos. 34, 35 and 36 are as follows: 2.90 percent, 44.97 percent and 62.97 percent respectively. It is evident from these results that the ampere efficiency increases rapidly as soon as the yellow stage of the anolyte is reached, which is indicated in experiments Nos. 34 and 35.

In experiments Nos. 37 and 38, the concentration of the anolyte was 0.2 gram of vanadic oxide per c.c. The electrodes were both carbon. For test No. 37 an anode current density of 48 amperes per sq. ft. (5.2 amp. per sq. dm.) was used. The temperature ranged from 85° to 94° C. The test ran for 7 hours and 22 minutes. The anode ampere efficiency was 40.57 percent. In experiment No. 38 an anode current density of 72 amperes per sq. ft. (8 amp. per sq. dm.) was used, the temperature ranging from 89° to 94° C. The deposit in this case did not adhere readily to the anode, most of it collecting in the bottom of the porous cup, and some being in the anolyte in colloidal form. The filtering of such a colloidal solution is extremely difficult, much of the precipitate passing through the filter. For this reason it was impossible to obtain an efficiency determination in experiment No. 38.

In experiment No. 40 a lead anode and a carbon cathode were employed. The concentration of the anolyte, which was in the porous cup, remained the same as in experiments Nos. 38 and 39. The anode current density averaged 16 amperes per sq. ft. (1.8 amp. per sq. dm.). The temperature varied from 87° to 94° C. Deposition on the anode started after three hours and twenty minutes. The anolyte at the start was faintly yellow and at the end was of orange color. The efficiency was not determined, as the anode deposit showed the presence of lead strongly. The lead in the product indicates that lead was dissolved from the anode and re-precipitated as lead peroxide with the vanadic oxide.

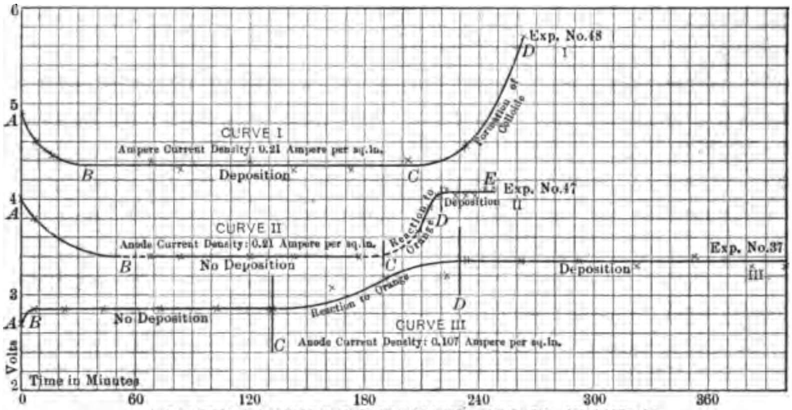
An endeavor was made to increase the ampere efficiency by hastening the formation of the yellow vanadium compound in solution by adding an oxidizing agent. What the orange yellow compound in the solution was could not be determined, but it was found that, on allowing the orange yellow solution to evaporate freely in the air, large orange-colored crystals were formed. These large crystals on analysis gave the following composition: V_2O_5 61.57 percent and moisture 27.44 percent. This composition corresponds very closely with the salt $Na_2O.2V_2O_5 + 9H_2O$. The crystals also corresponded in every other way with the properties attributed to this compound in the literature. The crystals weathered in moist air without losing their crystalline form. They are readily soluble in cold water, but difficultly so in hot, as they decompose, coating the crystals with a dark-red compound which is difficultly soluble, and prevents further action by the hot water. The salt is soluble in a solution of oxalic acid, giving a green color initially and ending with a blue, while CO_2 is given off, showing that the final solution is a reduction product.

While the main aim in experiments Nos. 41 to 46 was to obtain the orange-colored solution, in order to increase the current efficiency, the most startling observation was that, with only a few drops of a solution of hydrogen peroxide (3 percent by volume) the vanadic oxide (V_2O_5) was very readily dissolved by the theoretical amount of sodium hydroxide. In other words: instead of taking 22.72 grams of sodium hydroxide to dissolve 20.02 grams of vanadic oxide, it required only 8.97 grams of sodium hydroxide (98 percent pure), when 5 c.c. of a 3 percent hydrogen peroxide solution was added, or a saving of 153.3 percent of sodium hydroxide. The solution of sodium metavanadate thus obtained acted practically neutral.

Electrolytes containing 0.2 gram of vanadic oxide (V_2O_5), 0.09 gram sodium hydroxide and 0.05 c.c. of 3 percent hydrogen peroxide solution per c.c. were used in experiments Nos. 41 to 46. The electrodes employed were a platinum sheet anode and a carbon cathode. A porous cup was used to contain the vanadium solution. The anode current density varied from 7 to 30 amperes per sq. ft. (0.8 to 3.3 amp. per sq. dm.) and the temperature ranged from 89° to 99° C. In all of these tests the anode ampere efficiency was markedly increased by the use of the hydrogen peroxide solution, varying from 92.78 to 96.46 percent. The variation in current efficiency is due to the fact that in some instances not quite enough hydrogen peroxide had been added to convert all of the sodium metavanadate over into the orange yellow compound. Experiments Nos. 41 to 45 were run for three hours, while No. 46 ran for three hours and fifteen minutes.

In experiments Nos. 47, 48 and 49, current efficiency comparisons were made between the electrolysis of a solution prepared by dissolving vanadic oxide in sodium hydroxide, and solutions prepared by use of hydrogen peroxide and of sodium peroxide as oxidizing agents. The anolyte used in experiment No 47 contained 0.2 gram vanadic oxide and 0.22 gram sodium peroxide per c.c. The anolyte for experiment No. 48 contained 0.2 gram vanadic oxide, 0.09 gram sodium hydroxide and 0.05 c.c. hydrogen peroxide (3 percent by volume). The anolyte used for experiment No. 49 was prepared by using, instead of hydrogen peroxide, 0.25 gram sodium peroxide (Na_2O_2) per c.c. of electrolyte.

In all three experiments platinum sheet anodes and carbon cathodes were employed, and a porous cup was used to separate the anolyte and the catholyte. The catholyte was a dilute solution of sodium hydroxide. The anode current density was 30 amperes per sq. ft. (3.3 amp. per sq. dm.), and the temperature varied between 90° and 99° C. In test No. 47 the anolyte was strongly alkaline, in No. 48 neutral and in No. 49 slightly alkaline. In experiment No. 47 the orange color of the anolyte was obtained after three hours and forty minutes. A faint yellow color was observed after three hours and 10 minutes. It took, therefore, thirty minutes to obtain the full orange color after the first appearance of the faint yellow color, showing that when oxidation had started, the change from the faint yellow to the orange-colored solution progressed rapidly (see Curves I, II and III). The anode ampere efficiencies were as follows: 9.52 percent for experiment No. 47; 96.63 percent for experiment No. 48, and 85.89 percent for experiment No. 49. The anode deposit in each case was adherent and brick red in color. The analysis of the fused products was as follows: the deposit of No. 47, 97.99 percent V_2O_5; that of No. 48, 98.37 percent V_2O_5, and that of No. 49, 98.21 percent V_2O_5. By use of the chemical oxidizing agents (H_2O_2 and Na_2O_2) deposition of the hydrated vanadic oxide formed immediately on the anode, independently of electrolytic oxidation.



VOLT-TIME CURVES EXPERIMENTS, NOS. 37, 47 AND 48.

FIG. 2.

In experiments Nos. 50, 51 and 52, potassium chlorate ($KClO_3$), potassium permanganate ($KMnO_4$) and chloride of lime ($CaOCl.Cl$) were used as oxidizing agents on an anolyte of the same composition as was used in experiments Nos. 47, 48 and 49. The amounts of the oxidizing agents required for the complete dissolving of 20.02 grams of vanadic oxide (V_2O_5) in 100 c.c.

of water containing the theoretical amount of 98 percent sodium hydroxide (8.97 grams of NaOH) was 3 grams potassium chlorate, 0.008 gram of potassium permanganate and 0.52 gram of chloride of lime. In order to give the most effective oxidizing conditions at the anode, a platinum wire (No. 18 B. & S.) cathode was employed. The anode was a platinum foil. The anode current density used was 30 amperes per sq. ft. (3.3 amp. per sq. dm.) and the temperature varied from 76° to 90° C. Porous cups were used as diaphragms to separate the anolyte and the catholyte. The three tests were run in series for two hours. The anode ampere efficiencies were 50.48 percent for experiment No. 50; 35.11 percent for experiment No. 51, and 63.7 percent for experiment No. 52. In test No. 50 it took one hour to obtain the orange yellow anode solution. In experiment No. 51 it was difficult to say what happened, because of the purple color imparted to the anolyte by the potassium permanganate, while in experiment No. 52 it required thirty-five minutes to obtain the orange coloration. This lag in obtaining the orange-colored anode solution accounts for the low ampere efficiency. The anode deposits in experiments Nos. 50 and 52 were adherent and brick red in color, while the deposit of experiment No. 51 was dark reddish brown and showed a tendency to form a colloidal solution.

In experiments Nos. 54 to 57 the variation in concentration of the anolyte contained in a porous cup was considered. The current density was changed in experiment No. 57, and in all cases lead sheet anodes were employed, while the cathodes were carbon.

In tests Nos. 54 and 57 the concentration of the electrolyte was the same, 0.2 gram of vanadium oxide per c.c. The anode current densities were 30 and 15 amperes per sq. ft. (3.3 and 1.7 amp. per sq. dm.) respectively, while the temperature range was from 90° to 97° C. The concentration of the anolyte of experiments Nos. 55 and 56 was 0.10 and 0.075 gram vanadic oxide per c.c. respectively. The anode current densities were 30 amperes per sq. ft. (3.3 amp. per sq. dm.). The temperature at which No. 56 was run was 90° C., while that of the test No. 55 varied from 66° to 71° C. The anode deposits were all contaminated with lead, so that the anode ampere efficiency was not determined. However, the effect of concentration is observed by considering the weights of the deposits obtained in tests Nos. 54, 55 and 56, which are 5.6404; 3.2082 and 1.7146 grams respectively. That the anode ampere efficiency evidently decreases with the decrease in concentration of the vanadium anolyte is clearly shown by the yields obtained in the same length of time (2 hours and 15 minutes).

The concentration of the anolyte in experiments Nos. 58 and 59 was 0.2 gram of vanadic oxide per c.c. and 0.09 gram of sodium hydroxide per c.c. Ten c.c. of hydrogen peroxide (3 percent by volume) was added to the vanadium anolyte in test No. 58, and 0.25 gram of sodium peroxide to the anolyte of No. 59. Anolytes and catholytes were kept separated by the use of porous cups. The anode current density was 180 amperes per sq. ft. (20 amp. per sq. dm.) in each case, and the temperature ranged from 86° to 99° C. The anode ampere efficiency of test No. 58 was 84.22 percent, and that of test No. 59 was 80.29 percent. The tendency of the anode deposits in these two experiments was to form a colloidal solution, not so much of the vanadic oxide adhered to the anode as in cases where lower anode current densities were used. This to some extent explains the low current efficiency, as it was extremely difficult to obtain a perfect separation of the deposit and the solution by means of filtration, due to the colloidal state of some of the deposit itself. However, this loss would not make up the 12 percent difference between the yield of experiment No. 58 and experiment No. 48. The ampere efficiency evidently decreases with increase of the anode current densities above approximately 30 amperes per square foot (3.3 amp. per sq. dm.).

Experiments Nos. 60 to 62 involve chemically pure sodium metavanadate. The concentration was 0.2 gram of vanadic oxide per c.c. of water. A porous cup was used as a diaphragm to keep the anolytes and catholytes separated. The anode current density of Nos. 60 and 61 was 15 amperes per sq. ft. (1.7 amp. per sq. dm.), while in No. 62 the current density was 30 amperes per sq. ft. (3.3 amp. per sq. dm.). The temperature ranged from 87° to 99° C.

Experiment No. 60 indicates the length of time required to obtain the orange yellow solution. At the end of three hours the efficiency was only 8.76 percent, having taken two hours and 35 minutes before the orange yellow stage was reached. In test No. 61 the anolyte left from No. 60 was again electrolyzed for three hours and 56 minutes. For this length of time the anode ampere efficiency was 96.29 percent, indicating again the necessity of having the vanadate anolyte in its higher state of oxidation (the orange yellow compound) in order to obtain a high anode ampere efficiency.

In experiments Nos. 63 to 66, sodium carbonate, sodium peroxide, potassium hydroxide and ammonia were tested as solvents for vanadic oxide. These solutions were then subjected to electrolysis, using them as anolytes in porous cups. The anolyte of experiment No. 63 was made by dissolving 15 grams of vanadic oxide (V_2O_5) in 100 c.c. of water containing 11.45 grams of anhydrous sodium carbonate (Na_2CO_3). The concentration of the anolyte in respect to the vanadic oxide was 0.15 gram per c.c. In order to obtain complete solution of the vanadic oxide, 10 c.c. of hydrogen peroxide (3 percent by volume) was added. The solution was practically colorless. The anode current density used was 30 amperes per sq. ft. (3.3 amp. per sq. dm.). The temperature ranged from 82° to 94° C. The anode deposit obtained was adherent and brick red in color, the anode ampere efficiency being 53.37 percent. The run lasted for three hours and 15 minutes, two hours and 20 minutes being required to reach the orange yellow state of the anolyte. The anolyte of experiment No. 64 was prepared by dissolving 15 grams of vanadic oxide in 100 c.c. of water containing 5.22 grams of sodium peroxide (Na_2O_2). No addition of hydrogen peroxide was made, as the vanadic oxide dissolved in the theoretical amount of sodium peroxide. The sodium peroxide evidently acted as oxidizing agent. The anode current density and the temperature range was the same as in experiment No. 63. The anode deposit was of brick red color and adhered to the anode in layers. The anode ampere efficiency was 93.58 percent.

In experiment No. 65 the anolyte was prepared by dissolving 13.99 grams of vanadic oxide in 100 c.c. of water containing 9.23 grams of potassium hydroxide. Thirty c.c. of hydrogen peroxide (3 percent by volume) was added to get complete solution. The catholyte was dilute potassium hydrate. The conditions of electrolysis were the same as in experiments Nos. 63 and 64, but the test was run for only one hour and 35 minutes. A deposit weighing 7.7 grams was obtained on the anode. This deposit was so strongly contaminated by small yellow crystals, probably a complex potassium vanadate, that it was impossible to figure the anode efficiency. The small crystals at the anode were not an anode product, but separated from the anolyte, collecting to a great extent at the bottom of the porous cup. This is simply a case of super-saturation of the anolyte in respect to the crystalline compound. In experiment No. 66 an endeavor was made to prepare an anolyte, using ammonia as the solvent for vanadic oxide. This was found to be impossible, as even with an addition of 30 c.c. of hydrogen peroxide the practically insoluble ammonium metavanadate crystallized from the solution.

A series of tests were then run to investigate the effect of other oxides on the deposit. In each case 20 grams of vanadic oxide were mixed with 10 grams of the oxide in question. Mixtures of vanadic oxide with ferric oxide (Fe_2O_3), cuprous oxide (Cu_2O), mixtures of the two, manganese dioxide (MnO_2), lead peroxide (PbO_2), silica (SiO_2), lime (CaO), magnesia (MgO), alumina (Al_2O_3), zinc oxide (ZnO), arseneous oxide (As_2O_3) and with uranic oxide (UO_3). These mixtures of oxides were treated with 8.97 grams sodium hydroxide in 100 c.c. of water, containing 10 c.c. of hydrogen peroxide (3 percent by volume) similarly as when vanadic oxide was used alone. The solutions thus obtained were then used as anolytes in porous cups. The catholyte in each case was a dilute sodium hydroxide solution. The anodes were platinum foil and the cathodes carbon rods. The anode current densities were 30 amperes per sq. ft. (3.3 amp. per sq. dm.) and the temperature varied from 80° to 94° C. The anolyte in each case was the filtrate obtained by leaching the mixed oxides with the alkaline solution. These solutions were tested for the presence of the admixed element. The residue left on the filter paper was tested for vanadium.

When a mixture of ferric oxide and vanadic oxide were treated as above described, the filtrate obtained showed no trace of iron. The residue, after careful washing, showed only a trace of vanadium. The deposit obtained by electrolysis was brick red in color, adhered to the anode and was free from iron. The anode ampere efficiency was 96.17 percent.

Cuprous oxide is partly dissolved in the alkaline leaching solution forming in all probability the hydroxide which is soluble in the alkaline solution. It is highly improbable that copper metavanadate is in the solution, as this compound is only slightly soluble in alkaline solutions. The copper in the solution did not interfere with the anode deposit, no trace being found in the carefully washed anode product. The residue left after leaching and careful washing showed the presence of a small amount of undissolved vanadic oxide, indicating that the leaching was not quite complete. This in all probability is due to the fact that some of the alkali was used to form the hydrated oxide of copper. The deposit was normal and the anode ampere efficiency was 95.68 percent.

The anolyte obtained by leaching a mixture of the oxide of vanadium, iron (ic) and copper (ous) contained some copper; but no iron. The anode product of hydrated vanadic oxide contained neither iron nor copper after thorough washing. The residue from leaching the mixed oxides was washed, dried and tested for vanadium. Only a trace of vanadium could be detected. The anode deposit was normal, the anode ampere efficiency being 96.03 percent.

Manganese dioxide is attacked by the alkali leaching solution, forming either the manganese metavanadate with the vanadic oxide present or the hydroxide $Mn(OH)_2$ or both. These compounds are practically insoluble in alkalies. Only a trace of manganese could be detected in the anolyte. The residue left after leaching indicated that quite an amount of vanadic oxide had not been dissolved. The anode product showed no manganese, but it was darker in color than other anode products and somewhat slimy in appearance. This appearance of the anode product is undoubtedly due to the small amount of the manganese in solution. The amount of manganese in the deposit was, however, so small that it was impossible to detect it. The anode ampere efficiency was 80.79 percent. Evidently the presence of a small amount of manganese in the anolyte reduced the anode current efficiency.

Lead peroxide seemed to have some effect on the leaching. This compound forms alkali plumbates, soluble in alkalies, and also a vanadate. Some lead vanadate had evidently formed, as the leaching was incomplete. The anolyte after leaching indicated no abnormality, no lead being found in the filtrate, but some vanadium remained in the residue. The anode deposit was normal. The anode ampere efficiency was 79.13 percent.

Silica interferes materially with the leaching. Some silica enters the anolyte, but this does not affect the anode deposit. The residue after leaching has a yellowish-white appearance after washing and drying. On dissolving in acid the residue gives a red solution which shows vanadium strongly. The anode ampere efficiency was 69.96 percent. The anode deposit was normal.

Lime (CaO) resembles silica in its behavior. The anolyte showed the presence of calcium. The residue left from leaching has a yellowish-white appearance and dissolves in dilute acids with a red color, and gives a strong test for vanadium. This indicates that the residue is calcium vanadate. The anode ampere efficiency was 7.63 percent. This very low anode current efficiency proves that only very little vanadic oxide had been dissolved by the leaching solution. The anode product was brick red in color and adhered to the anode. After careful washing no calcium could be detected in the deposit.

Magnesia (MgO) forms a magnesium vanadate which is slightly soluble in the alkaline solution, and re-precipitates on heating. The residue left after leaching was yellowish-white in appearance and dissolved in dilute acids, forming a red-colored solution giving a strong vanadium reaction. The anode ampere efficiency was low, 26.82 percent. The deposit had a brick red color and adhered to the anode.

Alumina (Al_2O_8) behaved similarly to lime and magnesia, some entering the anolyte, while most of it stayed on the filter paper as a yellowish-white residue which dissolved in dilute acids, forming a red colored solution, and showed vanadium strongly. The anode ampere efficiency was 24.99 percent. The deposit was dark red, giving partly a colloidal solution and partly adherent deposit.

The oxide of zinc interferes only slightly with the leaching. Not all of the vanadic oxide was dissolved, but the vanadium reaction for the residue was much less than for silica, lime, magnesia or alumina. No zinc was detected in the anolyte. The anode ampere efficiency was 95.85 percent, the deposit being brick red and adhering well to the anode.

Arsenious oxide (As_2O_3) forms a greenish vanadate with vanadic oxide, which is slightly soluble in the leaching solution. The anode deposit obtained was gelatinous and adhered in part to the anode in a thin film, while some stayed in the anolyte in form of a colloid. The anode ampere efficiency was very low, and the deposit contained a large percentage of arsenic.

Uranic oxide (UO_3) prevented the complete extraction of vanadic oxide, some vanadic oxide remaining undissolved in the residue. No uranium could be detected in the anolyte, which had an oily appearance. The anode current efficiency was 96.20 percent, the deposit being brick red in color and adhering firmly to the anode.

Conclusions. The preliminary 33 experiments indicate that an oxidation takes place at the anode, the anode product which tends to form being of an orange red to brick red color. Platinum hydride is formed on a platinum cathode, which increases in amount as the current density increases, and as the time of the run is increased. The electrolyte changes from a faint yellow to an orange yellow, the color being due to the product formed at the anode redissolving. With increased concentration of vanadic oxide in the electrolyte, a red deposit formed on the anode, dissolving until the electrolyte was dark orange yellow, and then remaining as such on the anode. This suggested that if the anolytes and the catholytes were kept separate by porous partitions the yield of the anode product might be increased. This was done in experiments Nos. 34 to 66.

In experiments Nos. 34 to 40 it was apparent that the yield of the anode product of hydrated vanadic oxide materially increased as the orange coloration of the electrolyte increased. As the change from the practically colorless sodium metavanadate anolyte to that of the orange state was due to oxidation at the anode, hydrogen peroxide (3 percent by volume) was added to the sodium hydroxide solution in small quantities (5 to 10 c.c. per 100 c.c. of anolyte). The addition of the hydrogen peroxide accomplished the desired oxidizing effect, thus saving at least two hours and 18 minutes in obtaining the anode deposit, according to experiment No. 34, during which time no deposition took place in this test. The effect of an addition of hydrogen peroxide under the same current density conditions as in No. 34 is shown in experiment No. 46.

That a reaction is taking place in the anolyte in the course of electrolysis, affecting the deposition at the anode, may be observed from the volt time-curves Nos. I, II and III, for data see Table XIV. Three specific cases are considered. Curve I shows the effect of hydrogen peroxide on the anode deposition of hydrated vanadic oxide. The data is taken from experiment No. 48, using an anolyte containing per c.c. 0.2 gram of vanadic oxide, 0.09 gram sodium hydroxide and 0.05 c.c. of hydrogen peroxide (3 percent by volume). Deposition on the anode started practically as soon as the current passed, the color of the anolyte at the start being orange yellow. The voltage drop from A to B is due to the temperature rising to 92° C. From B to C normal anode deposition took place, the product adhering to the anode. From C to D the anode product changed to the colloidal state.

Curve II represents the action taking place in an anolyte containing per c.c. 0.2 gram of vanadic acid, 0.23 gram of sodium hydroxide and no hydrogen peroxide. The current density was kept constant at 30 amperes per sq. ft. (3.3 amp. per sq. dm.). From A to B a drop in voltage took place, due to the rise in temperature. From B to C no deposition occurred, the anolyte absorbing oxygen. At C the anolyte was in its higher state of oxidation, the color of the solution changing from light yellow to orange during the period C to D, due to the anolyte becoming saturated with the hydrated vanadic oxide. The deposition on the anode proceeded normally between D and E.

Curve III, experiment 37, illustrates the anode reactions which occur in an identical anolyte to that used in experiment No. 47, but at lower anode current density. The anode current density was kept constant at 15 amperes per sq. ft. (1.7 amp. per sq. dm.). During period A to B a slight rise in potential resulted, due to a slight drop in temperature (94° to 85° C.). During period B to C no deposition took place, but oxidation of the anolyte occurred similar to that during period B to C in experiment No. 47, Curve II. The period C to D, during which the anolyte was being saturated with the hydrated vanadic oxide, shows the saturation taking place when the anolyte changed from colorless to orange color, which is completed at D. Anode deposition took place between period D and E.

Table XIV.

Curve I.

Exp. No. 48. Dissolved 20.02 grams of vanadic oxide in 100 c.c. of water containing 8.97 grams of sodium hydroxide and 5 c.c. hydrogen peroxide (3 percent by volume), used as anolyte. Anode current density 0.21 amperes per sq. in. (30 amperes per sq. ft or 3.3 amperes per sq. dm.).

Curve II.

Exp. No. 47. 20.02 grams vanadic oxide dissolved in 100 c.c. of water containing 22.72 grams of sodium hydroxide, used as anolyte. Anode current density 0.21 amperes per sq. in. (30 amperes per sq. ft. or 3.3 amperes per sq. dm.)..

Curve III.

Exp. No. 37. 20.02 grams vanadic oxide dissolved in 100 c.c. of water containing 22.72 grams hydroxide, used as anolyte. Anode current density 0.107 ampere per sq. in. (15 amperes per sq. ft. or 1.7 ampere per sq. dm.).

Curve I		Curve II		Curve III	
Time in Minutes	Volts	Time in Minutes	Volts	Time in Minutes	Volts
0	4.9	0	4.0	0	2.65
8	4.6	8	3.8	7	2.85
9	4.45	60	3.4	15	2.85
51	4.4	15	3.4	20	2.85
15	4.3	37	3.4	30	2.85
37	4.4	23	3.4	30	2.85
23	4.3	30	3.4	30	2.85
30	4.3	30	3.65	30	3.05
30	4.4	15	3.92	30	3.18
30	4.55	15	4.05	30	3.2
30	5.7	5	4.1	12	3.55
		5	4.05	28	3.35
		5	4.05	30	3.35
		5	4.05	30	3.3
		5	4.1	30	3.4
		5	4.1	30	3.35
				30	3.35
				30	3.30

Curves II and III show clearly that a reaction takes place in the anolyte, and that the speed of this reaction may be increased by increasing the anode current density. By comparing the anode ampere efficiencies of experiments Nos. 37, 47 and 48, it is observed that in 48 the anode ampere efficiency was the highest, this being due to the yellow state of the anolyte at the start. This is also indicated by Curve I, deposition taking place at the anode from the very start of electrolysis, proving that the higher state of oxidation of the anolyte is essential for high anode current efficiency. These experiments and curves also show that the most suitable chemical oxidizing agent is hydrogen peroxide.

Another benefit is derived by the use of hydrogen peroxide as an oxidizing agent. Whereas, in experiment No. 34, it took 0.23 gram of sodium hydroxide per c.c. of water to dissolve 0.2 gram of vanadic oxide, it took only 0.09 gram of sodium hydroxide in experiment No. 46 to accomplish the same result. This means a saving of 153.3 percent of sodium hydroxide.

Experiments Nos. 41 to 46 show the effect of current density on the yield and on the anode ampere efficiency. The yield at the anode decreases as the current density decreases, while the anode ampere efficiency is only slightly influenced. The yield varies from 1.4903 grams vanadic oxide for anode current density of 7 amperes per sq. ft. (0.8 amp. per sq. dm.) to 6.2217 grams for anode current density of 30 amperes per sq. ft. (3.3 amp. per sq. dm.), the anode ampere efficiencies varying only between 92.78 percent and 96.29 percent, the higher anode current density giving the higher efficiency.

By comparing the results of electrolysis of a neutral, a slightly alkaline and a strongly alkaline anolyte (see experiments Nos. 47 and 48, also 49, it was found that the neutral anolyte gives the best yield and the highest anode ampere efficiency. A high anode ampere efficiency and a high yield of electrolytic vanadic oxide can only be obtained by using a non-alkaline oxidizing agent such as hydrogen peroxide, with the theoretical amount of sodium hydroxide (NaOH), in a practically neutral anolyte.

Hydrogen peroxide was found to be the most satisfactory chemical oxidizer for the preparation of the sodium metavanadate anolyte, as by its use a neutral anolyte may be obtained. Electrolytes thus prepared yielded high anode ampere efficiency.

Sodium peroxide was found to be less satisfactory than hydrogen peroxide as an oxidizer, as by its use a slightly alkaline anolyte resulted. The slight alkalinity reduced the anode ampere efficiency, and had a tendency to cause the anode deposit to become colloidal.

Potassium chlorate and chloride of lime, when used as chemical oxidizers for the preparation of the sodium metavanadate solution, gives an anolyte from which chlorine is liberated, which has a markedly deleterious effect on the anode deposits. Potassium permanganate was found to be an unsatisfactory oxidizer, as by its use the anode ampere efficiency was lowered, and the anode deposit of hydrated vanadic oxide was rendered impure.

The effect of concentration of the metavanadate anolyte was studied in experiments Nos. 54 to 57. The concentrations used were 0.075 to 0.2 gram vanadic acid per c.c. It was observed that, with a decrease in concentration, the yield of the anode deposit decreased. As lead anodes were employed, the anode ampere efficiency could not be obtained, because the anode product was contaminated with lead, and it was impossible to obtain a relatively pure vanadic oxide.

On comparing the effect of high anode current densities, 60 amperes per sq. ft. (6.6 amp. per sq. dm.), with anolytes containing 0.2 gram of vanadic acid per c.c., it was observed that the anode yield increased with increase in current density, whether hydrogen peroxide or sodium peroxide were used as an oxidizing agent. The increase in the anode yield by doubling the current was, however, not double that of the experiments in which 30 amperes per sq. ft. (3.3 amp. per sq. dm.) was used. Comparing experiments Nos. 42 and 58, it is observed that the yield in test 48 would be 5.3285 grams of vanadic oxide at the end of two hours and 40 minutes. In test 58 the yield for the same length of time was 9.6709 grams. That the yield in No. 58 was not double the one of 42 was due to the lower ampere efficiency of the first, which was only 84.22 percent, while that of the latter was 92.78 percent. By the use of sodium peroxide as an oxidizing agent the yield and the anode ampere efficiency were still less (see experiment No. 59), being 8.457 grams vanadic oxide; efficiency, 80.29 percent. In this last test the yield and anode ampere efficiency, besides being affected by the high current density, is furthermore influenced by the slight alkalinity of the anolyte, due to the sodium peroxide (Na_2O_2). In both experiments, Nos. 58 and 59, it was clearly shown that very high temperature (above 92° C.) and high anode current densities tend to make the anode deposit colloidal, especially so if the anolyte is slightly alkaline.

In experiments Nos. 60 to 62 it was found that chemically pure sodium metavanadate anolyte only gave a high ampere efficiency and a high yield of hydrated vanadic oxide after the anolyte had attained the orange yellow state—differing in this respect from experiments Nos. 34 to 40, in so far that the length of time required to obtain the orange yellow state was less. This higher anode efficiency of experiments Nos. 60 to 62 was due to the chemically pure sodium metavanadate solution being neutral, while in tests Nos. 34 to 40 the anolyte was strongly alkaline.

On comparing the solubility of vanadic oxide in solutions of sodium hydroxide, potassium hydroxide, ammonium hydroxide, to each of which hydrogen peroxide was added as the oxidizing agent, and sodium peroxide alone, it was found that the solution of sodium hydroxide plus hydrogen peroxide gave the most satisfactory results in every respect, giving the highest anode ampere efficiency and the best yield of electrolytic vanadic oxide. It was of value to compare the amounts of the alkalies required to dissolve the same amount of vanadic oxide, a solution of 8.97 grams of sodium hydroxide (98 percent pure) in 100 c.c. of water containing 5 c.c. of hydrogen peroxide completely dissolved 20 grams of vanadic oxide. In order to dissolve the same quantity of vanadic oxide it required 6.9 grams of 100 percent sodium peroxide in 100 c.c. of water; also a solution of 12.31 grams of potassium hydroxide in 100 c.c. of water containing 16 c.c. of hydrogen peroxide dissolved 20 grams of vanadic oxide. While it requires less sodium peroxide than of sodium hydroxide plus hydrogen peroxide, the great disadvantage of the first solvent is that its price is prohibitive, and the anode current efficiency is slightly lower, being 93.58 percent for the sodium peroxide solution, as compared with 96.63 percent for the sodium hydroxide plus hydrogen peroxide solution. Potassium hydroxide not only dissolves less vanadic oxide per sodium hydroxide equivalent, but it is also more expensive, and furthermore, it requires a larger amount of hydrogen peroxide. The product of electrolytic vanadic oxide from potassium hydroxide anolyte is contaminated with an insoluble potassium vanadate compound, which separates from the anolyte during the electrolysis. Ammonium hydroxide could not be used as solvent for vanadic oxide because, as soon as some vanadic oxide dissolved, it formed the insoluble ammonium metavanadate, which precipitated out and collected at the bottom of the receptacle.

Regarding the commoner associates of vanadium in ores, it may be said that the oxides of the alkaline earth metals (such as calcium and magnesium) interfere materially with the extraction of the vanadic oxide with solutions of sodium hydroxide containing hydrogen peroxide; they cause very poor extraction, and low anode ampere efficiencies. Iron oxide seems to have no ill effect, if present as ferric oxide (Fe_2O_3), but if present as a soluble salt the alkaline leaching solution precipitates the iron as hydroxide ($Fe(OH)_3$), and more leaching solution would be required to extract the vanadic oxide. A small amount of manganese in the anolyte causes the anode product to have a dark color, decreases the ampere efficiency and lowers the yield of electrolytic vanadic oxide.

Copper as oxide has very little effect on the extraction of vanadium by solutions of sodium hydroxide plus hydrogen peroxide. The extraction of the vanadic oxide is rapid, and it is due to this that copper does not enter the anolyte as soluble copper hydroxide. Lead peroxide interferes with the extraction, lowering the solubility of the vanadic oxide, but only a trace, if any, lead peroxide dissolved. The solution, on electrolysis, gave a pure anode product, but a low anode ampere efficiency. Alumina and silica behave similarly to the alkaline earth metal oxides, reducing the extraction and lowering the anode ampere efficiency. The anode product was slimy and very hard to handle. Zinc oxide slightly decreased the extraction, and only slightly affected the anode ampere efficiency. No zinc could be detected in the anolyte, and the anode deposit was normal in every respect. Arsenious oxide (As_2O_3) forms a complex compound with vanadic oxide, which is slightly soluble in the alkaline leaching solution. It caused a low anode ampere efficiency and a gelatinous anode deposit. Uranic oxide decreased the extraction of vanadic oxide to some extent, and gave an oily solution free from uranium. The anode ampere efficiency was high.

The low ampere efficiency is generally due to bad leaching giving an anolyte of too low a concentration in vanadic oxide. In every respect it is better to treat materials low in alkaline earths, silica and alumina. The presence of manganese oxide in very small amounts is deleterious. Iron, copper and zinc have little ill effect if present as oxides, the leaching being so rapid that none, or only a small amount, of these are dissolved by the alkaline leaching agent. Arsenic should be absent. In general it is better to treat a concentrated product containing vanadic oxide with only small amounts of impurities.

The only satisfactory anode is one of platinum. Lead contaminates the anode deposit, while on a carbon anode the product does not adhere. The cathode may be of iron, carbon, lead, copper or platinum. A slight increase in anode yield is obtained by making the cathode area small, so as to increase the oxidizing action at the anode. In all cases an insoluble porous diaphragm must be used in order to separate the anolyte and the catholyte, in order to obtain electrolytic vanadic oxide.

From approximately 60° C. up to 92° C. the anode deposit adheres firmly to the anode, if the anolyte is as nearly neutral as possible. Higher temperatures have a tendency to cause the formation of colloids. Similarly, very high current densities and high temperatures combined have the same effect. A third cause for the formation of colloids is the alkalinity of the anolyte. Finally, the colloidal state of the deposit is promoted by agitation of the anode solution.

In the 368 experiments performed, metallic vanadium was not obtained. The question naturally arises: "What is the cause of this"? Chemically it is known that vanadium oxide is extremely hard to reduce, even in the electric furnace and by the Goldschmidt Thermit process. The latter will, as a rule, reduce the oxides of metals like chromium, manganese and titanium with comparative ease, while the oxides of vanadium are reduced only with the greatest difficulty.

There is very little available information as to the heat of formation of vanadium salts. However, some attempts have been made by Mixter to determine the heat of formation of some of the vanadium oxides. The values obtained by Mixter are only approximations, and should not be considered otherwise. (Mixter: "Heat of Formation of Oxides of Uranium and Vanadium," American Journal of Science, **34**, 141-154). The deductions made to explain the non-deposition of metallic vanadium from aqueous solutions of its salts by means of the electric current are,

therefore, only theoretical. They are simply conclusions drawn from observed facts on other elements.

In the following table are given some heats of formation of oxides, sulphates, chlorides and fluorides.

HEATS OF FORMATION IN GRAM CALORIES.

Element	Oxides		Chlorides		Fluorides		Sulphates	
Silver	Ag_2O:	7000	$AgCl$:	29000	AgF:	22070	Ag_2SO_4:	167100
Copper	CuO:	37700	$CuCl_2$:	51400	CuF_2:	....	$CuSO_4$:	181700
Nickel	NiO:	61500	$NiCl_2$:	74700	NiF_2:	....	$NiSO_4$:	....
Tin	SnO:	70700	$SnCl_2$:	80900	SnF_2	....	....	....
Zinc	ZnO:	84400	$ZnCl_2$:	97400	ZnF_2:	....	$ZnSO_4$:	229600
Manganese ..	MnO:	90900	$MnCl_2$:	112000	MnF_2:	....	$MnSO_4$:	249400
Magnesium...	MgO:	143400	$MgCl_2$:	151200	MgF_2:	209500	$MgSO_4$:	300900
Iron	Fe_2O_3:	195600	$FeCl_3$:	96150	FeF_3:	....	....	....
Aluminium ..	Al_2O_3:	392600	$AlCl_3$:	161800	AlF_3:	....	....	....
Vanadium ...	V_2O_5:	441000	....	....	....	....	....	....
Vanadium ...	V_2O_3:	353200	....	....	....	....	....	....
Vanadium ...	VO:	104300	....	....	....	....	....	....

All values, except those for the vanadium compounds, are taken from Richards' Metallurgical Calculations: Vol. I, pp. 15-25.

It is known that elements like silver, copper and nickel are very easily deposited from their salt solutions. The heats of formation of the oxides of these elements are comparatively low, therefore the reducing power at the cathode necessary to decompose the salts is high enough to give the metal.

As the heat of formation of the oxides increases, more difficulty is encountered in obtaining metallic cathode deposits on electrolysis of the corresponding aqueous salt solutions. Such is the case with the oxides of tin, zinc, manganese and iron. With such oxides as aluminium oxide, deposits from aqueous salt solutions are practically unknown. It is therefore possible that, with vanadic oxide (V_2O_5) having a heat of formation greater than 441,000 gram calories, the reducing effect produced at the cathode by the electric current is insufficient to furnish the energy required to decompose a vanadic salt in aqueous solutions, which in general is greater for the salts than for that needed to decompose the oxides.

In some instances, too, elements are both acid and basic in their behavior. This is to some extent the case with tin and zinc, but

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much more so for manganese, aluminium and vanadium. These latter elements form manganates, aluminates and vanadates very readily. As the tendency to form these compounds increases, so does the possibility to form a metallic cathode product decrease, while the tendency to form anode products from neutral or alkaline electrolytes increases.

It is obvious that with the element vanadium one is not likely to obtain the metal as cathode deposit from aqueous salt solutions, due to the high heats of formation of the salts and to the great tendency shown by this element to form vanadates.

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Siegfried Fischer was born at Zurich, Switzerland, on December twenty-first, 1882. After completing the technical course at the Gymnasium at St. Gall, Switzerland, studied in the University of Zurich during 1900-1901. Studied Chemistry at the Polytechnicum of Zurich from 1901 to 1904. During the year 1904-1905 attended courses in chemistry at the University of Leipzig and the Polytechnicum of Charlottenburg. In 1905 entered Columbia University, and received the degree of B.S. in Chemistry in 1907. Received his degree of M.S. in Metallurgy from Lehigh University in 1915. Subject of Thesis: "The Vapor Tension of Metals below their Melting Points." The work was conducted under the direction of Dr. Joseph W. Richards. In 1915 registered for the Ph.D. degree at Columbia University, to do advanced work in metallurgy.

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